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Ferbam Residues on Canned Montmorency Cherries[1]

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In 1945 Adam, Dickinson, and Marsh (1) at the Long Ashton Station in England first called attention to some undesirable effects of dithiocarbamate residues on the quality of processed fruits. They reported that black currants sprayed with ferbam (ferric dimethyldithiocarbamate) contained 45 ppm of spray residue at harvest, and that the flavor, color, and storage life of the canned product was impaired. Currants canned in sirup contained 15 ppm of residue, but canned fruit pulp contained only traces. This decrease during processing may be explained by the ready decomposition of ferbam to carbon disulfide and other products when heated in the presence of fruit acids. In fact, this is the basis of the analytical method developed by Dickinson (3).

Subsequent reports from the Long Ashton Station (2, 6) have shown somewhat smaller concentrations of ferbam on black currants. However, the data indicate that as little as 1 ppm of residue in the canned product will impair its flavor and appearance, and accelerate the formation of hydrogen swells.

Recently Lowen (5) in this country reported that sour cherries sprayed with ferbam contained 3.6 ppm of residue on the raw fruit and 0.09 to 0.35 ppm after canning.

Since ferbam and other dithiocarbamate sprays are now used extensively as fungicides for sour cherries, it is important to determine what effect they have on the quality of the canned fruit. This report is limited to a study of ferbam residues on sour cherries, showing the concentration of residue on the raw and canned fruit and the quantity of added ferbam required to produce a change in flavor of the canned product.

Materials and Methods

Raw mature cherries were obtained from commercial orchards in Michigan and Pennsylvania. Canned cherries were prepared on a laboratory scale, usually six No. 2 cans per sample, using standard commercial procedures as described by Marshall et al. (7). Briefly, the procedure consisted of soaking the fruit overnight in cold water (50 to 57 degrees F), pitting with a Dunkley pitter, adding 16 ounces of fruit and 4 ounces of hot water to each No. 2 cherry enamel can, exhausting to 165 degrees F, closing, and cooking 12 minutes in boil-

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ing water. The cans were cooled, transported to the Eastern Regional Research Laboratory at Philadelphia, and stored at room temperature until opened for analysis or examination. Some of the fruit was canned at the Michigan State College fruit processing laboratory in 1949, and the remainder was processed during the 1950, 1951, and 1952 seasons at the Orrtanna, Pa. plant of Knouse Foods Coop., Inc.

In one experiment an alternate canning procedure was used. Details of this procedure are given under discussion of results.

In the experiments with added ferbam, a weighed amount of a commercial spray formulation analyzing 74.9 per cent of active ingredient was placed in the bottom of each can before weighing in the pitted cherries preparatory to canning. Calculations of ferbam required were based on the net can contents (cherries plus water).

Color was evaluated in terms of optical density determined on an aliquot of the juice surrounding the canned fruit. Marshall et al. (7) have indicated that this procedure gives a valid measure of the color of canned cherries. The filtered juice was diluted 1 : 5 with distilled water and the per cent transmittance in a 22 mm test tube was measured at 440 mμ on a photoelectric filter-photometer.

The presence of off-flavors was determined organoleptically by either a triangle or a paired method, using a taste panel of 9 to 16 persons trained to detect the type of off-flavor involved. The panel usually spent two sessions on each sample so that sufficient judgments (18 to 32) were obtained to facilitate analysis of the results. The significance of the results was determined by the formula recommended by Boggs and Hanson (3).

The samples were analyzed for ferbam by the Dickinson (6) method with the exception that the cherries were comminuted in a Waring blendor before steam distillation. This treatment removed most of the dissolved or trapped carbon disulfide so that only the undecomposed ferbam was determined. Carbon disulfide and ferbam were determined separately by a modification of the Dickinson method. The modified procedure consisted of sampling the juice and cherries at the time the taste tests were begun (approximately 30 minutes after the can was opened) and making the samples alkaline to prevent ferbam decomposition. Fifty per cent sodium hydroxide was added dropwise to juice samples until they were definitely alkaline and the whole transferred to the distillation unit. The samples of cherries were immersed in 0.2 N sodium hydroxide solution and transferred without comminution to the distillation unit. These operations were done as quickly as possible and with as little agitation of the sample as possible. The unit was not swept with nitrogen as in the Dickinson method and twice the quantity of copper reagent was added to the receiver before the carbon disulfide was steam distilled from the alkaline solution. After distillation of the carbon disulfide, the contents of the distillation unit were made acid by adding an excess of solid citric acid. A second portion of chloroform was added and the carbon disulfide resulting from the decomposition of the ferbam was distilled into a fresh receiver. The carbon disulfide content of both the juice and cherries was calculated to ppm. of ferbam.

RESULTS

Ferbam Residues on Fresh and Canned Cherries:—The ferbam analyses of three samples of fresh cherries and five samples of canned fruit are shown in Table 1. The concentration of residue on the fresh

TABLE 1—FERBAM RESIDUE ON CHERRIES FROM COMMERCIAL ORCHARDS.

Orchard and State	No. of ferbam sprays used	Ppm ferbam found	
		Fresh	Canned
McLachlan, Mich.	4	—	0.5
	4 with wax	—	0.5
Morrison, Mich.	4	—	0.4
	4 with wax	—	0.4
Morrison, Mich.	6	2.1	0.7
Garrettson, Pa.	3	2.5	—
Orner, Pa.	2	1.4	—
Pape, Pa.			
Ave.		2.0	0.5

cherries was much lower than that reported for black currants (1). This might be due to the difference in surface area per unit weight of the two fruits. The values on the fresh fruit were somewhat lower, and those on the canned samples slightly higher than the values reported by Lowen (5). The canned samples were normal with respect to flavor and color. It is apparent from the present data that much of the ferbam residue present on the fresh fruit is lost during processing. This agrees with the results previously reported by others (1, 6).

An attempt was made to follow the loss of ferbam at various steps in the processing of cherries. The results given in Table 2, show that most of the loss occurs during canning. Since ferbam is readily decomposed to carbon disulfide and other products in the presence of mild acid and heat, it is not surprising that appreciable losses occur during heat processing.

TABLE 2.—CHANGES IN FERBAM RESIDUES DURING PROCESSING OF SOUR CHERRIES.

Description of sample	Ppm ferbam found
Raw cherries	2.1
After soaking 23 hrs at 50–54° F.	1.6
Canned sample	0.7

Effect of Added Ferbam:—It is highly important to know what concentration of ferbam residue is necessary to produce an off-flavor in canned cherries. Since none of the samples of ferbam sprayed cherries gave canned products with impaired flavor or color, it was necessary to can fruit with added ferbam. The results of this experiment are shown in Table 3. In general, only 10 to 15 per cent of the added ferbam was recovered from the canned samples. This low recovery was due to loss of carbon disulfide during processing and during preparation of the sample for analysis. There is also some loss of carbon disulfide in the head space gases when the cans are opened.

The red color of the canned cherries was not decreased by the addition of as much as 82 ppm of ferbam during canning. This result does not agree with the report by Adam et al. (1) that 45 ppm of ferbam caused a loss of color of canned currants.

TABLE 3.—EFFECT OF ADDED FERBAM ON FLAVOR AND COLOR OF CANNED CHERRIES.

Ppm ferbam added	Ppm ferbam found	Off-flavor present	Optical density[a]
0	0.0	None	0.282
0.8	0.3	None	0.321
3.3	—[b]	None	0.328
8.2	0.7	None	0.310
33.0	—[b]	Slight[c]	0.321
82.0	11.8	Very strong	0.329

[a]Optical density = 2—Log T where T is per cent transmittance near 440 mu.
[b]Not analyzed.
[c]Results of triangle test significant at P = .05.

The presence of off-flavors was determined by a taste panel using a triangle test. In the first series of tests 33 ppm of added ferbam gave an off-flavor detectable by this method.

The following season additional samples of cherries were canned with 10 ppm and 20 ppm of added ferbam. The samples were opened after six weeks' storage at room temperature and submitted to a taste panel trained to detect the particular off-flavor involved. The sample containing 10 ppm did not have a sufficient degree of off-flavor to enable the panel to detect it. The panel detected an off-flavor in the 20 ppm sample by both a triangle test and a paired test. (see Table 4). The off-flavor caused by 20 ppm of added ferbam was not an unpleasant taste but was identified by most tasters as a bland flavor or lack of flavor. An untrained taster could not detect an undesirable flavor even at 40 ppm.

TABLE 4.—TASTE PANEL EVALUATION OF CHERRIES CANNED WITH 10 ppm AND 20 ppm ADDED FERBAM

	Number of judgments	Number correct	Number required for significance P = .05
10 ppm—triangle test	32	15	16
20 ppm—triangle test	18	10*	10
20 ppm—paired test	26	21*	20

*Significant at P = .05.

The off-flavor is undoubtedly caused by a decomposition product of ferbam, since ferbam itself has no flavor, either alone or when mixed with cherry juice. There is strong evidence that CS_2 causes the off-flavor. Cherries canned with 200 ppm of ferbam have a distinct odor and taste resembling CS_2. When the sample was boiled in an open pan the odor and off-flavor disappeared.

An experiment was designed to determine separately the amounts of CS_2 and residual ferbam in cherries canned with 20 ppm of added ferbam. No. 2 cans of commercially canned cherries were used. The cans were opened and the can contents poured into empty No. 2 cherry enamel cans containing 11.4 mg ferbam. The cans were processed, cooled, and stored two weeks prior to analysis.

Two standard commercial canning procedures were compared (Table 5). The difference between the two procedures is largely in the extent of heating before closing the cans. The older and more common procedure, called exhausting, is to heat the can contents in a water bath until the center can temperature reaches 165 degrees F. The lids are then sealed on and the cans are given an additional cook until they

TABLE 5.—EFFECT OF METHOD OF CANNING ON DECOMPOSITION OF FERBAM (20 ppm ADDED FERBAM).

	Exhaust Cook 12 min	8 min (total 20)	Cook 15 min (no exhaust)	
	CS_2 (as ferbam)	Residual ferbam	CS_2 (as ferbam)	Residual ferbam
Total ppm found	6.7	3.9	3.3	7.9
Per cent in juice	23.0	32.0	0.0	62.0
Per cent in cherries	77.0	68.0	100.0	38.0
Added ferbam recovered (per cent)	34	19	17	39
Total recovery (per cent)	53		56	

reach 195 degrees F center can temperature. The alternate method is to remove air from the pitted cherries by applying a mechanical vacuum to the cans and to add water before the vacuum is released. Head space vacuum is obtained by partially replacing the air by a steam jet just before closing the cans. The cans were then cooked to a center temperature of 195 degrees F. It is obvious that this latter procedure provided less chance of losing volatile decomposition products, such as carbon disulfide, during heat processing.

The results show that 53 to 56 per cent of the added ferbam was recovered as either carbon disulfide or residual ferbam. The first procedure, which is more commonly used commercially, involved a total heating time of 20 minutes and decomposed 81 per cent of the added ferbam. The concentration of CS_2 in the cherries and juice was 6.7 ppm.

The second canning procedure involved only 15 minutes total heating time and decomposed 61 per cent of the added ferbam. The concentration of CS_2 (calc. as ferbam) in the cherries and juice was 3.4 ppm. This is the concentration that was barely detectable organoleptically. The two canning procedures showed no appreciable difference in the per cent recovery of added ferbam, but did show a difference in the proportions of CS_2 and residual ferbam. Presumably 10 ppm of added ferbam would have produced an off-flavor in cherries canned by the first procedure (20 min. heating).

Effect on Can Corrosion:—No extensive study was made of the effect of ferbam on can corrosion, but the following observations indicate that the problem is not a serious one. Cans of ferbam sprayed cherries after two years' storage at room temperature still had 5 inches (Hg) vacuum in the head space. Cans of cherries with 10 ppm of added ferbam showed no acceleration in loss of vacuum after one year at room temperature, and it required approximately three years for them to lose all their vacuum and to become hydrogen springers. Storage for two years without complete loss of vacuum would be considered adequate for canned cherries.

Several cans containing 33 and 82 ppm of added ferbam were examined after twelve months' storage and showed no evidence of corrosion of the tinplate. These results do not agree with the reports by Adam et al. (1, 2) that ferbam accelerates can corrosion.

Discussion and Summary

Ferbam is decomposed during canning by the combination of heat and mild acid to produce carbon disulfide which is probably responsible

for the off-flavor of the canned product. The concentration of spray residue on ferbam sprayed cherries from commercial orchards was approximately 2 ppm. The concentration in the canned product was 0.5 ppm. Experiments with added ferbam indicate that 3.3 ppm of CS_2 (calculated as ferbam) is required to give an off-flavor detectable by a trained taste panel. This would require 10 to 20 ppm of added ferbam. Relatively high concentrations of added ferbam had no effect on can corrosion nor color of the canned cherries.

It is concluded from the present data that ferbam spray residues on Montmorency cherries as a result of normal spray practice have no adverse effect on the color, flavor, or storage life of the canned product.

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